

NAC2-678
IN-92-2-2
(C) 1995
1

INTERSTELLAR ALCOHOLS

S. B. CHARNLEY,^{1,2} M. E. KRESS,^{2,3} A. G. G. M. TIELENS,² AND T. J. MILLAR⁴

Received 1994 February 14; accepted 1995 January 30

ABSTRACT

We have investigated the gas-phase chemistry in dense cores where ice mantles containing ethanol and other alcohols have been evaporated. Model calculations show that methanol, ethanol, propanol, and butanol drive a chemistry leading to the formation of several large ethers and esters. Of these molecules, methyl ethyl ether ($\text{CH}_3\text{OC}_2\text{H}_5$) and diethyl ether $[(\text{C}_2\text{H}_5)_2\text{O}]$ attain the highest abundances and should be present in detectable quantities within cores rich in ethanol and methanol. Gas-phase reactions act to destroy evaporated ethanol and a low observed abundance of gas-phase $\text{C}_2\text{H}_5\text{OH}$ does not rule out a high solid-phase abundance. Grain surface formation mechanisms and other possible gas-phase reactions driven by alcohols are discussed, as are observing strategies for the detection of these large interstellar molecules.

Subject headings: ISM: abundances — ISM: clouds — ISM: molecules — molecular processes

1. INTRODUCTION

Methanol (CH_3OH), the simplest alcohol, is widely observed in both the gas phase and the solid phase of the dense interstellar medium (e.g., Irvine, Goldsmith, & Hjalmarsen 1987; Tielens & Allamandola 1987). Infrared observations show that it can be a significant fraction of molecular ice mantles relative to water (Tielens & Allamandola 1987). Gas-phase abundances relative to H_2 range from $\sim 10^{-9}$ in cold, dark clouds (Friberg et al. 1988) to 10^{-7} to 10^{-6} in the hot molecular cores associated with regions of massive star formation (Menten et al. 1988) and ultracompact H II regions (Churchwell 1990). It is now accepted that the highest gas-phase methanol abundances are found in regions where ice mantles have recently evaporated from warm dust grains. Gas-phase processes cannot produce the observed abundances of 10^{-7} or more (Millar, Herbst, & Charnley 1991a) and solid state chemical reactions on grains are necessary.

Ethanol ($\text{C}_2\text{H}_5\text{OH}$), second in the homologous series, is not observed in dark clouds (Irvine et al. 1987) but it is present in star-forming regions with gas-phase abundances estimated to lie in the range of $\sim 10^{-8}$ (Millar et al. 1988) to 10^{-6} (Turner 1991). The lowest abundances cannot be reproduced in gas-phase chemistry models (Herbst & Leung 1989; Millar et al. 1991a), even under the most favorable conditions (Charnley, Tielens, & Millar 1992). Observational spectra of the C-H stretching band near $3.4 \mu\text{m}$ in the diffuse interstellar medium bear a striking resemblance to that of solid *n*-butanol (*n*-butyl alcohol) at 10 K (Sandford et al. 1991). Thus, the observational evidence is that interstellar CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ can be formed by grain surface chemistry much more efficiently than by gas-phase chemistry, and that even higher alcohols could be present in grain mantles.

Recent theoretical work has demonstrated that the chemistry of hot molecular cores is active (Charnley & Tielens 1992; Charnley et al. 1992; Caselli, Hasegawa, & Herbst 1993;

Charnley & Millar 1994): evaporated ices drive selected gas-phase pathways depending upon the relative molecular composition of the ices. This scenario can explain the hot core abundances of complex molecules such as dimethyl ether $[(\text{CH}_3)_2\text{O}]$, methyl formate (HCOOCH_3), ketene (CH_2CO) and acetaldehyde (CH_3CHO), as well as the molecular differentiation between individual cores. Dimethyl ether and methyl formate are not the products of grain surface chemistry but are formed by ion-molecule reactions from evaporated methanol; the former by the well-known self-alkylation process (e.g., Karpas & Mautner 1989) and the latter by alkyl transfer to formaldehyde from protonated methanol. These observational, theoretical, and experimental considerations lead one to inquire as to the nature of astrochemistry in sources where large quantities of alcohols are present.

In this paper we adopt the view of Charnley et al. (1992) that only specific classes of molecule, in particular the alcohols, are produced in grain mantles and evaporated in hot core regions. In this way, we are able to produce quantitative models of the subsequent chemistry and suggest particular observational tests of the theory. In § 2 we outline the theoretical model and describe an ion-molecule chemistry, based on experimental measurements involving methanol, ethanol, propanol, butanol, and formaldehyde, as well as the complex molecules that may be formed from them. In § 3, we present model results of calculations of hot core chemistry under conditions appropriate to the Compact Ridge component of Orion A. In § 4, we discuss the viability of our assumptions concerning alcohol formation on grains, other possible routes to gas-phase complexity attainable via alcohol chemistry, and briefly outline prospects for observing large organic molecules. Our conclusions are summarized in § 5.

2. THEORY

2.1. Model

We have employed a chemical kinetic model to study hot core chemistry (see Brown, Charnley, & Millar 1988) when ices are evaporated containing significant quantities of ethanol, isopropyl alcohol (*i*- $\text{C}_3\text{H}_7\text{OH}$), *n*-propyl alcohol (*n*- $\text{C}_3\text{H}_7\text{OH}$), *t*-butyl alcohol (*t*- $\text{C}_4\text{H}_9\text{OH}$), and *n*-butyl alcohol (*n*- $\text{C}_4\text{H}_9\text{OH}$), as well as methanol and formaldehyde. We adopted the approach taken by Charnley et al. (1992) to calculate the

¹ Astronomy Department, University of California, Berkeley, CA 94720.

² Space Science Division, NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035.

³ Physics Department, Rensselaer Polytechnic Institute, Troy, NY 12180.

⁴ Mathematics Department, UMIST, P.O. Box 88, Manchester, England M60 1QD, UK.

chemical evolution in the hot static gas. We consider an initial state where all the heavy atomic and molecular material is incorporated in mantle molecules and where the gas phase consists of molecular hydrogen and helium atoms along with their related molecular and atomic ions. The molecular ice mantles are composed of H_2O , CO , N_2 , O_2 , CH_4 , C_2H_4 , C_2H_6 , H_2CO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $i\text{-C}_3\text{H}_7\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$, $t\text{-C}_4\text{H}_9\text{OH}$, and $n\text{-C}_4\text{H}_9\text{OH}$. Evaporation of these ice mantles drives a hot gas-phase chemistry and the evolution of molecular complexity.

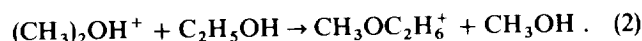
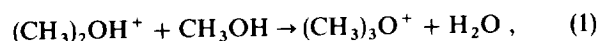
We consider a dense core with $n_{\text{H}} = 2 \times 10^6 \text{ cm}^{-3}$ and temperature of 100 K, conditions appropriate for the Orion Compact Ridge (Blake et al. 1987). The mantle abundances suggested by Charnley et al. (1992) yield good agreement for the Compact Ridge abundances of several organic molecules and we take this source as prototypical of other methanol-rich hot cores. For the calculations of this paper, the input mantle abundances for the first nine molecules listed above were from Table 1 of Charnley et al. (1992); that is, 2×10^{-5} , 1×10^{-4} , 7×10^{-5} , 2×10^{-7} , 1×10^{-7} , 8×10^{-8} , 1×10^{-8} , 1.2×10^{-7} , and 1×10^{-6} , respectively. These values were fixed in all models. To span the range of observational estimates, we performed three calculations with input ethanol abundances of 1×10^{-6} , 1×10^{-7} , and 1×10^{-8} , and present results for the first two. Note that having no ethanol in the ices leads to ethanol gas-phase abundances of less than 10^{-11} (Charnley et al. 1992). In each of the three models the total input propanol and butanol abundances were taken to be respectively 10 and 100 times less than that of ethanol, divided equally between the two isomeric forms considered here. The adopted values are based upon the reasonable (but unverifiable) assumption that the mantle abundances of higher homologues fall off with increasing size.

2.2. Interstellar Alcohol Chemistry

The basic gas-phase chemistry employed is well documented (Millar et al. 1991a, b; Charnley et al. 1992). For the chemistry of the higher alcohols we have used the experimental results of Karpas & Mautner (1989). The basic reaction process is alkyl transfer from a protonated alcohol to a neutral one leading to the protonated pure or mixed ether (i.e., containing identical or

different alkyl groups). The principal ion-molecule reactions involving interstellar alcohols and the rate coefficients adopted are listed in Table 1. Figure 1 shows schematically the main reactions of interest in the coupled methanol-ethanol chemistries. Each of HCO^+ , H_3O^+ , and CH_3OH_2^+ can protonate a higher neutral alcohol but only CH_3OH is protonated by H_3^+ . Ethanol is destroyed by H_3^+ (Millar et al. 1991b) and we assume, pessimistically, that this is also the case for higher alcohols; it is certainly true for dimethyl ether and diethyl ether (Lee, Drucker, & Adams 1992). The reactions leading from $n\text{-C}_3\text{H}_7\text{OH}$ and $n\text{-C}_4\text{H}_9\text{OH}$ to the pure ethers, $(n\text{-C}_3\text{H}_7)_2\text{O}$ and $(n\text{-C}_4\text{H}_9)_2\text{O}$, are analogous to those depicted for CH_3OH in Figure 1, except that their protonated forms do not proton transfer to other alcohols. The normal isomers of propanol and butanol apparently do not form mixed ethers (Karpas & Mautner 1989); however, in the case of the isomers $i\text{-C}_3\text{H}_7\text{OH}$ and $t\text{-C}_4\text{H}_9\text{OH}$, their protonated forms can react with CH_3OH leading to the production of mixed ethers. The chemistries of $i\text{-C}_3\text{H}_7\text{OH}$, and $t\text{-C}_4\text{H}_9\text{OH}$ are each analogous to that depicted for ethanol in Figure 1.

Karpas & Mautner (1989) showed that as the degree of alkylation (i.e., the total number of alkyl groups in the reacting system) increased, the rate coefficients of alkyl transfer reactions tended to decrease. We have thus ignored many reactions which contain three or more alkyl groups such as those between protonated ethers and alcohols. Of these, two reactions that could be important are



Reaction (2) is endothermic (Karpas & Mautner 1989) and proton transfer is preferred. Neglect of reactions like reaction (1) greatly reduced the number of complex species added to the original reaction network. We have, however, included three reactions involving three alkyl groups: reactions of protonated mixed ethers with the neutral alcohols from which they were derived (reactions 4, 5, & 6 of Table 1). These reactions lead to the pure ether and are potentially important in determining the relative abundances of pure and mixed ethers. Note that CH_3OH_2^+ does not react with $\text{C}_2\text{H}_5\text{OH}$ or higher alcohols to

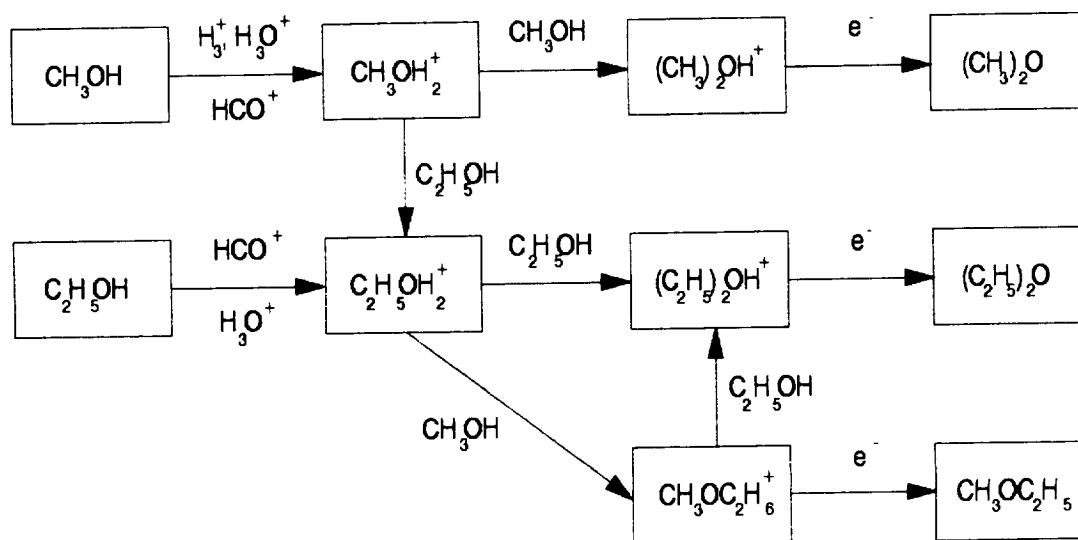


FIG. 1.—Schematic of the principal ion-molecule reaction paths leading from methanol and ethanol to ethers

TABLE 1
 ION-MOLECULE REACTIONS INVOLVING METHANOL, ETHANOL, PROPANOL, AND BUTANOL

No.	Reaction				$k(\text{cm}^3 \text{s}^{-1})$	Reference
1.....	$\text{C}_2\text{H}_5\text{OH}_2^+$	$+ \text{H}_2\text{CO}$	$\rightarrow \text{HCOOC}_2\text{H}_6^+$	$+ \text{H}_2$	$1.70(-11)$	1 ^a
2.....	$\text{C}_2\text{H}_5\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$\rightarrow \text{CH}_3\text{OC}_2\text{H}_6^+$	$+ \text{H}_2\text{O}$	$3.00(-11)$	1 ^b
3.....	$\text{C}_2\text{H}_5\text{OH}_2^+$	$+ \text{C}_2\text{H}_5\text{OH}$	$\rightarrow (\text{C}_2\text{H}_5)_2\text{OH}^+$	$+ \text{H}_2\text{O}$	$6.80(-11)$	2
4.....	$\text{CH}_3\text{OC}_2\text{H}_6^+$	$+ \text{C}_2\text{H}_5\text{OH}$	$\rightarrow (\text{C}_2\text{H}_5)_2\text{OH}^+$	$+ \text{CH}_3\text{OH}$	$1.00(-11)$	2 ^c
5.....	$i\text{-C}_3\text{H}_7\text{OCH}_3^+$	$+ i\text{-C}_3\text{H}_7\text{OH}$	$\rightarrow (i\text{-C}_3\text{H}_7)_2\text{OH}^+$	$+ \text{CH}_3\text{OH}$	$1.50(-11)$	2 ^c
6.....	$t\text{-C}_4\text{H}_9\text{OCH}_3^+$	$+ t\text{-C}_4\text{H}_9\text{OH}$	$\rightarrow (t\text{-C}_4\text{H}_9)_2\text{OH}^+$	$+ \text{CH}_3\text{OH}$	$2.25(-11)$	2 ^b
7.....	$n\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ \text{H}_2\text{CO}$	$\rightarrow n\text{-C}_3\text{H}_7\text{OOCH}_2^+$	$+ \text{H}_2$	$1.00(-11)$	2 ^a
8.....	$n\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ n\text{-C}_3\text{H}_7\text{OH}$	$\rightarrow (n\text{-C}_3\text{H}_7)_2\text{OH}^+$	$+ \text{H}_2\text{O}$	$1.00(-10)$	2
9.....	$i\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ \text{H}_2\text{CO}$	$\rightarrow i\text{-C}_3\text{H}_7\text{OOCH}_2^+$	$+ \text{H}_2$	$4.30(-11)$	1 ^a
10.....	$i\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$\rightarrow i\text{-C}_3\text{H}_7\text{OCH}_3^+$	$+ \text{H}_2\text{O}$	$3.00(-11)$	1 ^c
11.....	$i\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ i\text{-C}_3\text{H}_7\text{OH}$	$\rightarrow (i\text{-C}_3\text{H}_7)_2\text{OH}^+$	$+ \text{H}_2\text{O}$	$6.10(-10)$	2
12.....	$n\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ n\text{-C}_4\text{H}_9\text{OH}$	$\rightarrow (n\text{-C}_4\text{H}_9)_2\text{OH}^+$	$+ \text{H}_2\text{O}$	$1.50(-10)$	2
13.....	$n\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ \text{H}_2\text{CO}$	$\rightarrow n\text{-C}_4\text{H}_9\text{OOCH}_2^+$	$+ \text{H}_2$	$1.00(-11)$	1
14.....	$t\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$\rightarrow t\text{-C}_4\text{H}_9\text{OCH}_3^+$	$+ \text{H}_2\text{O}$	$3.00(-11)$	1 ^c
15.....	$t\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ \text{H}_2\text{CO}$	$\rightarrow t\text{-C}_4\text{H}_9\text{OOCH}_2^+$	$+ \text{H}_2$	$1.00(-11)$	1
16.....	$t\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ t\text{-C}_4\text{H}_9\text{OH}$	$\rightarrow (t\text{-C}_4\text{H}_9)_2\text{OH}^+$	$+ \text{H}_2\text{O}$	$6.60(-10)$	2
17.....	CH_3OH_2^+	$+ \text{C}_2\text{H}_5\text{OH}$	$\rightarrow \text{C}_2\text{H}_5\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$3.00(-11)$	2 ^b
18.....	CH_3OH_2^+	$+ \text{C}_2\text{H}_5\text{OH}$	$\rightarrow \text{C}_2\text{H}_5\text{OCH}_3^+$	$+ \text{H}_2\text{O}$	$0.00(+00)$	2
19.....	CH_3OH_2^+	$+ i\text{-C}_3\text{H}_7\text{OH}$	$\rightarrow i\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$3.00(-11)$	1
20.....	CH_3OH_2^+	$+ n\text{-C}_3\text{H}_7\text{OH}$	$\rightarrow n\text{-C}_3\text{H}_7\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$3.00(-11)$	1
21.....	CH_3OH_2^+	$+ n\text{-C}_4\text{H}_9\text{OH}$	$\rightarrow n\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$3.00(-11)$	1
22.....	CH_3OH_2^+	$+ t\text{-C}_4\text{H}_9\text{OH}$	$\rightarrow t\text{-C}_4\text{H}_9\text{OH}_2^+$	$+ \text{CH}_3\text{OH}$	$3.00(-11)$	1

NOTE: $a(-b) = a \times 10^{-b}$.

REFERENCES.—(1) this work; (2) Karpas & Mautner 1989.

^a Reaction observed by Karpas & Mautner; their estimate of k , our product distribution.

^b Reaction observed by Karpas & Mautner; our estimate of k .

^c Reaction postulated by Karpas & Mautner; our estimate of k .

form protonated mixed ethers, and that instead proton transfer occurs. As CH_3OH is the most abundant alcohol in hot cores, we have included only reactions between it and the protonated isomers of propanol and butanol. We have not considered any reactions between complex species derived from ethanol, $i\text{-C}_3\text{H}_7\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$, $t\text{-C}_4\text{H}_9\text{OH}$, or $n\text{-C}_4\text{H}_9\text{OH}$.

Table 1 shows that rate coefficients for alkyl transfer increase with increasing alcohol size and degree of branching. Experiments (Karpas & Mautner 1989) and theory (Herbst & Dunbar 1991) show that the rate coefficients for radiative association increase with reactant size. We have ignored radiative association reactions since the actual abundances of the molecules in whose chemistry it may play a significant part, propanol and butanol, are unknown. Detailed consideration of such extremely complex molecules as might result from this route is beyond the scope of this study. Important, and tentative, inclusions in Table 1 are that, in analogy with the reaction believed to lead to interstellar methyl formate (e.g., Millar et al. 1991b), that is,



we have assumed that reactions of protonated higher alcohols with formaldehyde, for example,



lead to the protonated ester. Recombination of the molecular ion produced in reaction (4) should form ethyl formate (HCOOC_2H_5). We have been unable to find experimental verification of this assumption and note that Karpas & Mautner (1989) give that the products of reactions (3) and (4) include $\text{CH}_3\text{OCH}_2^+$ and $\text{C}_2\text{H}_5\text{OCH}_2^+$, respectively. Inclusion of these molecular ions and their chemistries increases the complexity of the reaction network and, as we are motivated to explore the

possibility of producing large molecules by reactions analogous to reaction (3), we retain the reactions of Table 1 but note that our results may be compromised beforehand.

Finally, to the reactions of Table 1 we have added appropriate destruction reactions for complex organic molecules. Protonation of large neutral molecules by H_3^+ , HCO^+ , and H_3O^+ proceeds with a rate coefficient of $2\text{--}3 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$. Charge transfer by H^+ and C^+ occurs at a rate $3 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$. Destruction by He^+ , with a rate coefficient of $3 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$, is assumed to cleave the large organic molecules to yield several simple hydrocarbons in the product distribution and so to limit the development of molecular complexity. Dissociative recombinations occur at a rate of $1.5 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$. For the protonated ethers and esters derived from ethanol, propanol, and butanol, equal branching ratios were assumed for the channel yielding the original alcohol and the channel producing the associated neutral ether or ester. The total number of reactions added to the original network was 171.

3. RESULTS

Understanding the chemistry driven by alcohols is straightforward (Fig. 1). Cosmic-ray ionization leads to H_3^+ , HCO^+ , and H_3O^+ in the core and these protonate the neutral alcohols. The ion-molecule chemistry then proceeds by reactions between protonated and neutral alcohols (principally self-alkylation), leading to protonated pure and mixed ethers; dissociative recombination then produces the neutral ether molecule. As the core evolves the alcohols are gradually destroyed and the derived ethers and esters concomitantly disappear.

Figure 2 shows the evolution of the chemistry driven by evaporated methanol and that of the principal molecular ions; the evolution is the same in each of the models described below. The calculated abundances of $(\text{CH}_3)_2\text{O}$ and

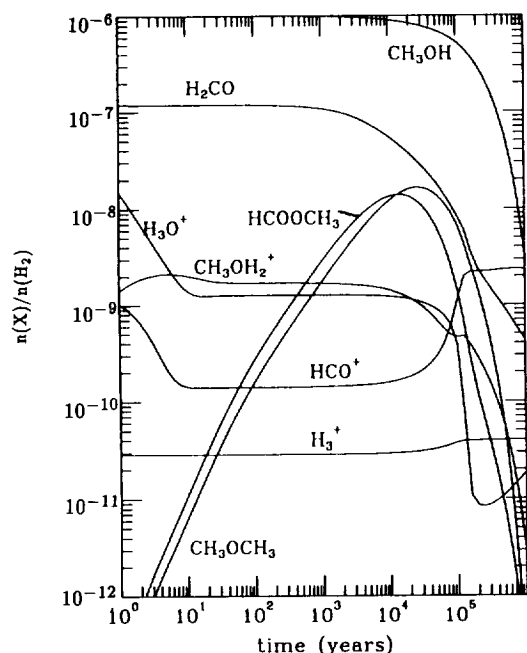


FIG. 2.—Chemical evolution of the methanol-formaldehyde chemistry and the major molecular ions. The evolution is almost identical in all models as the input CH_3OH and H_2CO abundances are the same in each. The physical conditions were $n_{\text{H}} = 2 \times 10^6 \text{ cm}^{-3}$ and $T = 100 \text{ K}$. The mantles were injected into the gas at $t = 0$. See text for further details.

HCOOCH_3 can be used to monitor the evolution of complexity in hot cores; for example, in the Orion Compact Ridge these molecules appear to be peaking in abundance (Charnley et al. 1992), implying an age of 10^4 – 10^5 yr. Figures 3 and 4 show the results of two model calculations in which the mantle abundances of ethanol, propanol, and butanol differ by a

factor of 10. As expected, the abundances of the derived species are proportional to the input abundance of the relevant alcohol. The chemistries of the higher alcohols evolve roughly on a similar timescale as the methanol chemistry although, since they are destroyed and not protonated by H_3^+ , the higher alcohols are more rapidly removed than methanol. Apart from being the only isomeric forms that react with CH_3OH_2^+ , *i*- $\text{C}_3\text{H}_7\text{OH}$ and *t*- $\text{C}_4\text{H}_9\text{OH}$ react faster with their protonated counterparts than do the corresponding *n*-isomers (Table 1). This results in higher abundances of species containing the isopropyl and tertiary butyl groups in the models. On the one hand, the abundance of methanol is much higher than that of the other alcohols in the models, enhancing the production rate of mixed over pure ethers. On the other hand, the reaction rate coefficients involved in the production of the pure ethers is larger than those for mixed ethers. These two opposing effects balance for the models shown in Figure 3 and so the abundances of diethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$] and methyl ethyl ether ($\text{CH}_3\text{OC}_2\text{H}_5$) are comparable. At lower input abundances for ethanol (Fig. 4) $\text{CH}_3\text{OC}_2\text{H}_5$ always dominates. A similar argument holds for the pure and mixed ethers formed from the branched isomers of propanol and butanol.

We now apply these theoretical results to the interpretation and molecular phenomenology of hot core sources. The maximum observed abundances of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ are determined by grain surface chemistry; given our basic premise, it is tautological to state that both propanol and butanol may also be present in hot cores. Considering the higher alcohols first, and taking a fractional abundance of 10^{-11} as a lower limit, then, unless the mantle abundances of propanol and butanol are significantly higher than we have assumed, only a few large ethers can conceivably be formed at detectable abundances. These are (*i*- C_3H_7) $_2\text{O}$ (di-isopropyl ether) and *i*- $\text{C}_3\text{H}_7\text{OCH}_3$ (methyl isopropyl ether); *t*- $\text{C}_4\text{H}_9\text{OCH}_3$ (methyl *t*-butyl ether) is the most abundant

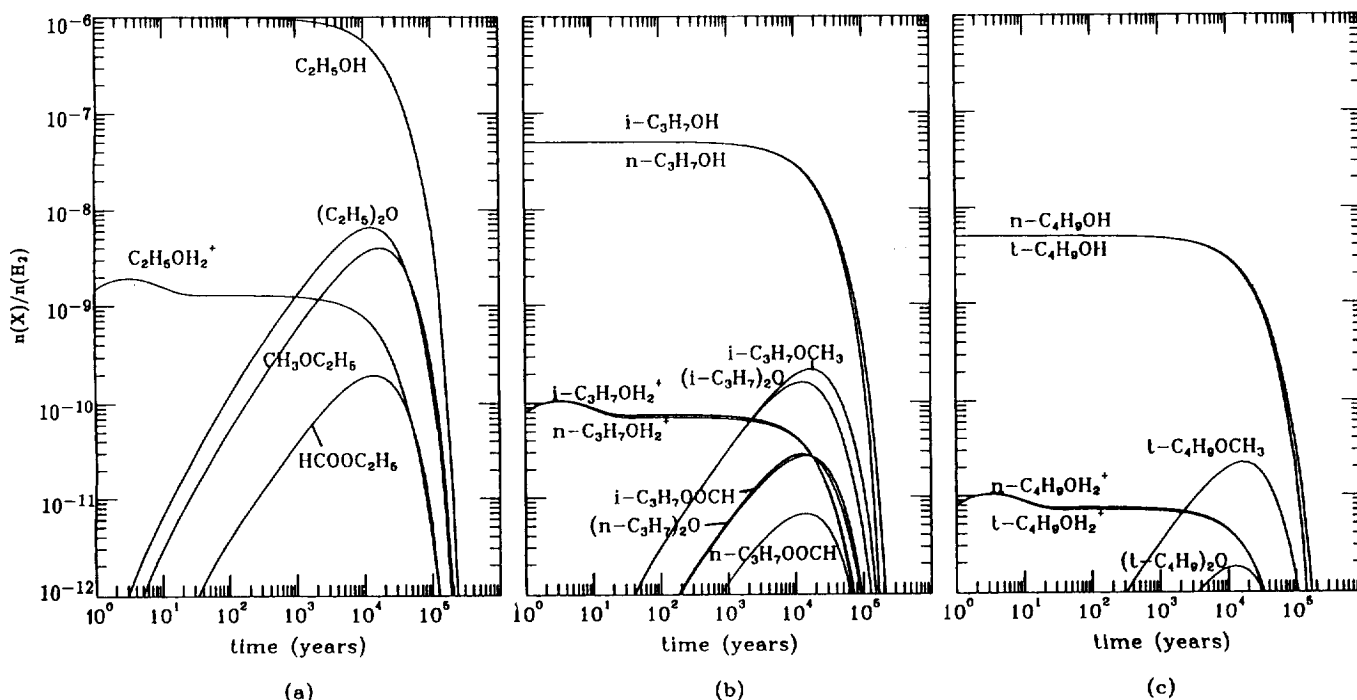


FIG. 3.—Chemical evolution of the (a) ethanol, (b) propanol, and (c) butanol chemistries in the hot core model depicted in Fig. 2. The input abundances of each alcohol were 1×10^{-6} , 1×10^{-7} , and 1×10^{-8} , respectively.

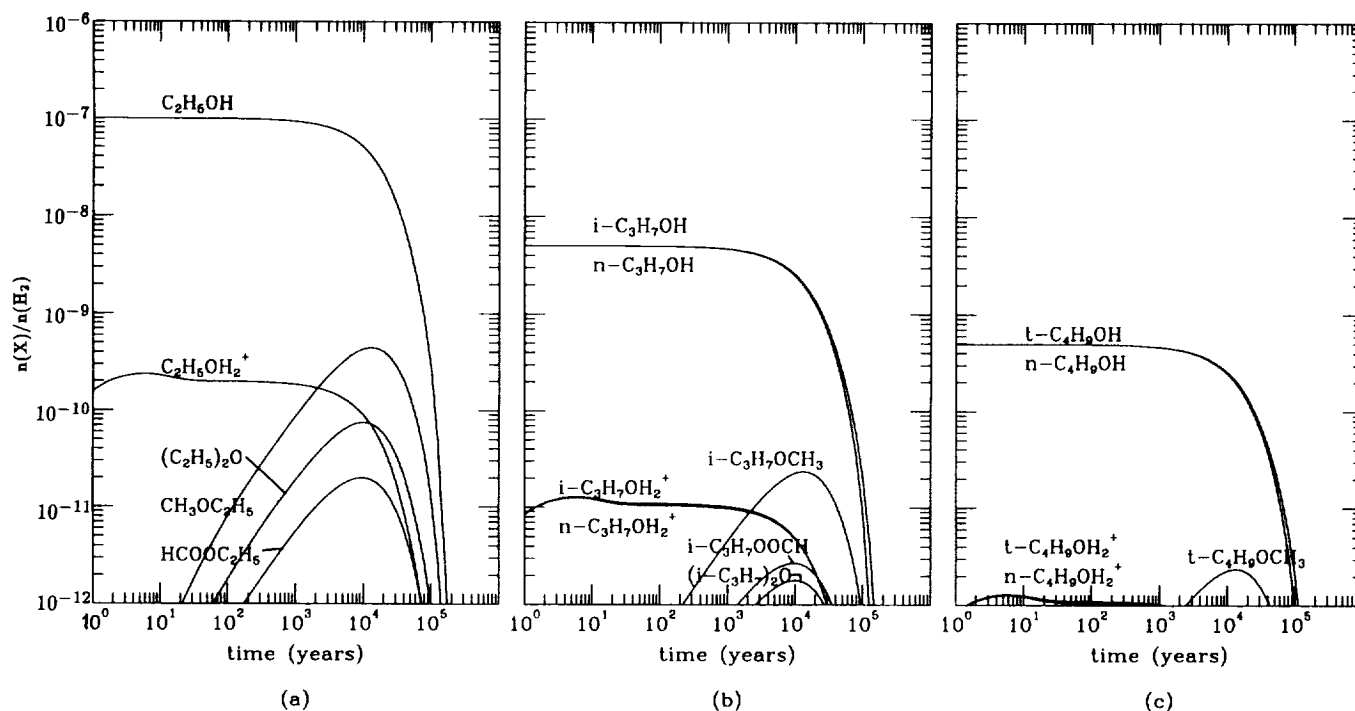


FIG. 4.—Same as Fig. 3 except that the input abundances of ethanol, propanol, and butanol were 1×10^{-7} , 1×10^{-8} , and 1×10^{-9} , respectively

complex molecule formed from butanol. We expect that these alcohols may play only a limited part in producing (detectable) molecular complexity in the gas phase. By contrast, for ethanol, a range of abundance estimates are available ($\sim 10^{-6}$ to 10^{-8} ; Blake et al. 1987; Millar et al. 1988, 1995; Turner 1991), and our calculations demonstrate that this molecule can produce appreciable abundances of $(C_2H_5)_2O$ and $CH_3OC_2H_5$ over most of this range. Of the esters considered in this study only $HCOOC_2H_5$ (ethyl formate) attains a significant abundance, and this in the models containing the most ethanol (see Fig. 3).

In the Compact Ridge the observed $(CH_3)_2O$ abundance is about 10^{-8} (Blake et al. 1987), implying that the time since mantle evaporation lies in the range $\sim 10^4$ – 10^5 yr (Fig. 2). If Turner's high estimate of the ethanol abundance ($\sim 10^{-6}$; Turner 1991) is correct, both $CH_3OC_2H_5$ and $(C_2H_5)_2O$ should be present in this source with abundances of a few times 10^{-9} . If the ethanol abundance of Blake et al. (1987) is more appropriate ($\sim 10^{-11}$), then the models predict abundances below detection limits. In W51 M, Millar et al. (1988) found that $(CH_3)_2O$ has the same abundance as in the Compact Ridge but the C_2H_5OH abundance is 10^{-8} . Millar et al. interpreted these observations with a model in which the products of grain surface chemistry are sensitive to the H-atom abundance. However, it is difficult to use this model to predict the ethanol/dimethyl ether ratio in particular sources, so we interpret the observations in terms of our detailed numerical calculations. The transient nature of the ethanol-driven chemistry leads to two possible interpretations of the W51 M observations. First, in a model which initially contains 100 times more ethanol than presently observed in W51 M (i.e., Fig. 3), $(CH_3)_2O$ and C_2H_5OH attain observed abundances after about 10^5 yr and both $CH_3OC_2H_5$ and $(C_2H_5)_2O$ have abundances of $\sim 2 \times 10^{-10}$. The important point here is that ethanol may originally have been very abundant (in the evapo-

rated mantles) but has been subsequently destroyed by gas-phase reactions. Despite much lower observed ethanol abundances, the daughter products may still be present. Clearly, sources with very large ethanol abundances should show the largest ether abundances. Second, if ethanol is injected from grains at its observed abundance in W51 M, then we calculate that the peak ether abundances are severely depressed. In particular, the peak $CH_3OC_2H_5$ abundance falls from $\sim 4 \times 10^{-9}$ (Fig. 3) to $\sim 4 \times 10^{-11}$; all species derived from the higher alcohols have abundances much lower than $CH_3OC_2H_5$. Detection of either $CH_3OC_2H_5$ or $(C_2H_5)_2O$ in W51 M would confirm the importance of ethanol as a grain mantle constituent.

4. DISCUSSION

We now address the question of the formation of interstellar alcohols by solid state chemical reactions, the detectability of complex organic molecules, and other aspects of alcohol chemistry.

4.1. Formation of Alcohols on Grains

We briefly discuss three possible reaction pathways, with particular reference to the synthesis of methanol and ethanol, where observation clearly demands such a process.

First, we consider the importance of H and O atom attack on species containing carbon double and triple bonds. Such reactions generally have *activation barriers* but quantum tunneling or thermally promoted reactions are still possible on grain surfaces (Tielens & Hagen 1982; Tielens 1992). Hydrogen atom addition to CO may lead to CH_3OH and matrix isolation studies show that HCO is readily formed at 10 K (van IJzenendoorn 1985; Bohn, Allamandola, & Sandford 1995). Formation of higher alcohols by this route requires intermediate oxidation of alkyl radicals. For example, H addition to C_2H_2 with

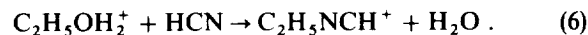
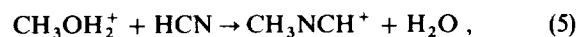
oxidation of either the vinyl or ethyl radicals could produce ethanol (Tielens 1992). Acetylene is predicted to be highly abundant ($\approx 10^{-6}$) on grain surfaces within dense condensations by direct accretion from the gas phase (Brown et al. 1988). Evans, Lacy, & Carr (1991) have observed large abundances of C_2H_2 in the Orion hot core where its origin must be attributed to evaporation from grains (Charnley et al. 1992). Accretion of other acetylenic compounds, followed by hydrogenation and oxidation, are plausible surface routes to various higher alcohols. Hot core observations of methyl acetylene (CH_3CCH) and diacetylene (C_4H_2), possible precursors of propanol and butanol, are not available. Although CH_3CCH is detected in a number of molecular clouds (Irvine et al. 1981; Askne et al. 1984; Andersson, Askne, & Hjalmarsson 1984), and is sometimes seen toward hot core sources (e.g., G34.3), it is always found to have a low rotational temperature—there is no observational evidence that CH_3CCH is a “hot core” molecule (Ziurys & McGonagle 1993). Grain formation of ethanol and dimethyl ether was considered by Millar et al. (1988). It is now clear that $(CH_3)_2O$ is formed by gas-phase chemistry. In the qualitative model devised by Millar et al. (1988), the proposed route to C_2H_5OH can be discounted since it relies on an unrealistically low abundance of H atoms in the accreting gas.

Second, we consider *radical-radical surface reactions*. At dust temperatures of 10 K, only O, C, and N atoms can diffuse rapidly enough to participate in the surface chemistry. Radicals, such as OH and CH_3 , are expected to remain trapped in their residence site (Tielens & Hagen 1982) and hence are efficiently hydrogenated to water and methane, with methanol production very limited (see Tielens & Hagen 1982; Brown & Charnley 1990). At higher dust temperatures (~ 20 K), OH and CH_3 radicals can diffuse on a grain surface and their reaction may lead to methanol. This scenario predicts variations in the concentration of methanol in interstellar grain mantles depending on the accretion temperature of the grains (cold: water-rich; warm: methanol-rich). Accretion, oxidation, and hydrogenation of CH_3 would also be important in methanol production; formation of higher alcohols would require the oxidation of accreted ethyl, propyl, and butyl radicals and is therefore contingent on the existence of a well-developed hydrocarbon chemistry in the accreting gas.

Third, we consider *diffusion-controlled reactions in bulk molecular ices*. The icy mantles of cold dust grains in molecular clouds contain the products of H atom addition surface reactions: H_2O , NH_3 , CH_4 , H_2S , as well as other molecules present by accretion or by hydrogenation of accreted molecules: CO, N_2 , O_2 , C_2H_2 , C_2H_4 , C_2H_6 . Ultraviolet photolysis of these simple ices, for example by the Prasad-Tarafdar flux (Prasad & Tarafdar 1983), can lead to atoms and simple radicals being frozen in the amorphous ice matrix at dust temperatures of 10 K: OH, CH_3 , NH_2 , CN, C_2H_3 , C_2H_5 (see Hagen, Allamandola, & Greenberg 1979; Greenberg 1982). Warming of these ices in star-forming regions will promote radical diffusion, annealing, and the formation of more complex molecules (Agarwal et al. 1985; Schutte 1988). Reactions of the hydroxyl radical with methyl and ethyl radicals could produce methanol and ethanol. If, during formation of a cold dense core, H addition to C_2 , C_3 , and C_4 , along with other partially hydrogenated carbon chain species, is indeed efficient (Hasegawa, Herbst, & Leung 1992), then UV photolysis and warming of ices containing the resulting aliphatic hydrocarbons such as propane (C_3H_8) and butane (C_4H_{10}) could produce higher alcohols.

4.2. Other Alcohol-driven Reactions

This work has been concerned primarily with ion-molecule reactions involving simple alcohols and formaldehyde. It is natural to inquire what complex molecules could be driven by reactions of $CH_3OH_2^+$ and $C_2H_5OH_2^+$ with other abundant mantle molecules such as NH_3 and HCN. Hydrogen cyanide can be formed by gas-phase reactions in hot cores (Charnley et al. 1992) but is also probably abundant on grains prior to evaporation (Brown et al. 1988), as witnessed by the presence of DCN in hot cores (Brown & Millar 1989; Mangum, Plambeck, & Wootten 1991). Two reactions of interest are



Both reactions (5) and (6) have been studied in the laboratory and have measured rate coefficients of $1.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, respectively (Mautner & Karpas 1986). Two interesting possibilities exist, depending upon whether reactions (5) and (6) lead to isocyanides or to cyanides. Mautner & Karpas (1986) have argued that protonated isocyanides are formed and hence we would expect, depending on the branching ratios for dissociative recombination, that CH_3NC and C_2H_5NC would be viable species for detection in hot cores. In this context, we note that CH_3NC has been tentatively detected in TMC-1 by Irvine & Schloerb (1984) and claimed in Sgr B2 by Cernicharo et al. (1988). An alternative possibility is that, following formation of the protonated isocyanides, isocyanide-cyanide isomerization occurs (see Defrees, McLean, & Herbst 1985) and that the ultimate neutral products are CH_3CN and C_2H_5CN . More CH_3NC measurements of methanol-rich cores are needed. The nondetection of isocyanides in hot cores would support the second possibility. Alkyl cation transfer reactions may in fact account for most of the organic molecules seen in hot cores (Charnley 1995). For systems involving a large number of atoms, radiative association can become significant in the formation of large molecular ions (Herbst & Dunbar 1991), leading to increased molecular complexity. However, the rate coefficients involved in radiative association are usually a strong function of temperature, indicating that, to a first approximation, such processes can be neglected in hot gas chemistry.

4.3. Detection Prospects for Large Organic Molecules

It is of some interest to consider the possibility of detecting the large molecules predicted here to be present in hot cores. Microwave studies of large molecules are difficult. For large species such as these, centrifugal distortion is important and hence transition frequencies cannot be easily predicted from rotational constants but have to be measured directly. The small rotational spacing leads to large partition functions, particularly at hot core temperatures, and the intensity in any line is small, more so for nonlinear molecules. However, we can get an indication of the expected antenna temperatures of some large molecules by noting that, for optically thin emission, the intensity of a given transition is proportional to $\mu_b^2/Q(T_{rot})$, where μ_b is the *b*-type electric dipole moment (much larger than the *a*-type dipole for all molecules considered here). $Q(T_{rot})$ is the partition function at rotational temperature T_{rot} and is proportional to $(ABC)^{-0.5}$, where *A*, *B*, and *C* are the rotational constants of the species concerned. We can compare the intensities of transitions from the synthesized esters and ethers to those in ethanol by assuming that all molecules have the same

column and T_{rot} . Then for similar transitions, we have

$$\frac{T_A(X)}{T_A(\text{EtOH})} = \frac{\mu_b(X)}{\mu_b(\text{EtOH})} \left[\frac{ABC(X)}{ABC(\text{EtOH})} \right]^{0.5} \quad (7)$$

Using rotational constants and dipole moments from Hayashi & Kawad (1974, 1975, 1980), we find $T_A(X)/T_A(\text{EtOH}) = 0.3$, 0.1, and 0.1 for $X = \text{methyl ethyl ether}$, diethyl ether , and $\text{methyl propyl ether}$, respectively. Since our numerical results indicate that, for times less than a few times 10^4 yr, the abundances of large ethers and esters are much less than ethanol, it is clear that their detection will prove a formidable challenge to radioastronomers. B. E. Turner (private communication) has searched unsuccessfully for methyl ethyl ether, dimethyl ether, and ethyl formate in Orion-KL, finding upper limits to the column densities of about 10^{14} cm^{-2} . In W51 M, he finds the upper limit to the diethyl ether abundance is about (2–10)% that of ethanol, consistent with the results shown in Figures 3 and 4 if hot core ages are less than a few times 10^4 yr. More sensitive searches for diethyl ether might prove rewarding.

Interstellar molecules can also be detected through their fundamental vibrations in the infrared, which can appear in absorption against a bright background source (i.e., a luminous protostar). Saturated aliphatic ethers, for example, have two characteristic strong absorption bands in the range $1150\text{--}1060 \text{ cm}^{-1}$ ($8.70\text{--}9.45 \mu\text{m}$), due to the C—O—C stretching vibration (Shimanouchi 1978). The asymmetric mode around 1130 cm^{-1} ($8.85 \mu\text{m}$) is generally the strongest. For pure ethers (i.e., diethyl ether), the C—O—C stretching mode occurs at about 1110 cm^{-1} ($9.0 \mu\text{m}$) and the asymmetric mode is absent. These modes are very strong with an expected integrated intensity of $3 \times 10^{-17} \text{ cm molecule}^{-1}$. Assuming a thermal line width at 300 K, this strength translates into a column density of 10^{12} cm^{-2} in a rotational state for an optical depth of 0.05 in one specific rovibrational transition. Hence, for a total absorbing hot core column density of 10^{23} cm^{-2} this corresponds to an abundance of 10^{-11} in one rovibrational state. Emission in the rovibrational lines requires high densities and high temperatures of the gas. The critical density for rovibrational transition is on the order of $\sim 10^{13} \text{ cm}^{-3}$ while the excitation energy is $\sim 300 \text{ K}$, so that for typical hot core densities and temperatures not much collisional excitation is expected. Molecules in a dense molecular clump near a luminous protostar will resonantly “scatter” the incident IR radiation from the dust photosphere. Hence, the molecular rovibrational transitions will appear as “emission” lines on top of the IR dust continuum from that clump. Typically, we can expect to see an optical depth of unity in the dust into the clump. The best wavelength region to search is then probably the dust opacity gap in the $5\text{--}8 \mu\text{m}$ region. At $8 \mu\text{m}$, outside of the silicate feature, this corresponds to a hydrogen column density of $1.5 \times 10^{23} \text{ cm}^{-2}$. Adopting the absorption strength for diethyl ether as a typical strength, we find a molecular scattering optical depth of $0.5X_{-9}$ per unit of dust extinction optical depth, where X_{-9} is the molecular abundance in the particular level under consideration in units of 10^{-9} . The scattered flux from a clump at a distance, d , from a protostar with a luminosity, L_* , and color temperature, T_c , is given by (Pendleton, Tielens, & Werner 1990)

$$F_s(\lambda) = \frac{L_*}{16\pi d^2 \sigma T_c^4} B(\lambda, T_c) \tau_{\text{scat}} \Omega, \quad (8)$$

with Ω the solid angle of the clump and τ_{scat} the scattering optical depth. Adopting $L_* = 10^5 L_\odot$, $d = 0.02 \text{ pc}$, ($10''$ at 500 pc for Orion), $T_c = 500 \text{ K}$, $\Omega = 3 \times 10^{-10} \text{ sr}$ ($2''$ radius), and $\tau_{\text{scat}} = 0.5$ yields $F_s = 6 \times 10^{-16} \text{ W cm}^{-2} \mu\text{m}^{-1}$. For comparison, assuming the clump is optically thick in the dust and a typical temperature of 150 K , the dust continuum flux at $8 \mu\text{m}$ is calculated to be $7 \times 10^{-16} \text{ W cm}^{-2} \mu\text{m}^{-1}$. Hence, the line-to-continuum ratio is about unity. The dust continuum is, of course, very sensitive to the adopted dust temperature and hence the distance between clump and star. It may actually be advantageous to move relatively far from the illuminating star where dust temperatures are low and thus much lower molecular scattering optical depths could be detected. Absorption or emission IR spectroscopy—depending on geometry—may be the best way to obtain secure identifications of large interstellar molecules in hot cores (via their rovibrational spectra).

5. CONCLUSIONS

We have demonstrated that evaporation of molecular ice mantles containing simple alcohols drives molecular complexity leading to the formation of pure and mixed ethers, as well as some esters. We find that the abundances and relative proportions of pure and mixed ethers depend upon the initial mantle abundance of the precursor alcohol. Ethers formed from branched alcohols are more abundant than those formed from the unbranched form, assuming that both isomeric forms were equally abundant in the ices. We find that $\text{CH}_3\text{OC}_2\text{H}_5$, $(\text{C}_2\text{H}_5)_2\text{O}$, and HCOOC_2H_5 could be abundant in methanol/ethanol-rich hot cores like the Orion Compact Ridge and W51 M. The abundances of species derived from higher alcohols are less certain due to lack of observational constraints, but, in hot cores where propanol and butanol are present, $i\text{-C}_3\text{H}_7\text{OCH}_3$ and $(i\text{-C}_3\text{H}_7)_2\text{O}$ will be the most abundant species, followed by $i\text{-C}_3\text{H}_7\text{OOCH}$, $(n\text{-C}_3\text{H}_7)_2\text{O}$, and $t\text{-C}_4\text{H}_9\text{OCH}_3$, respectively. An important issue is that, as hot core chemistry is of a highly transient nature, the observation of an alcohol (e.g., $\text{C}_2\text{H}_5\text{OH}$) at a moderate abundance does not exclude it from having been much more abundant in the original ices. The presence of detectable abundances of $\text{CH}_3\text{OC}_2\text{H}_5$ and $(\text{C}_2\text{H}_5)_2\text{O}$ would confirm that $\text{C}_2\text{H}_5\text{OH}$ can attain large solid-state abundances. If the most pessimistic model considered here is the most appropriate, then $\text{CH}_3\text{OC}_2\text{H}_5$ will be the only derived molecule with an abundance greater than 10^{-11} .

In conclusion, searches for several of the large organic molecules considered in this paper should be focused on those sources known to be rich in ethanol. Observations are required to measure the relative abundances and distributions of methanol and ethanol in a larger sample of hot core sources. Many relevant reactions have been studied in the laboratory and several assumptions, concerning rates and products, have recently been experimentally confirmed (Smith, Spänel, & Millar 1994; Lee et al. 1992). Further laboratory studies are needed to determine reaction products and to explore the possible importance of alcohol-driven ion-neutral chemistries. Theoretical studies of grain surface chemistry, and comparison of the results with laboratory ice analog experiments, are needed to discover the formation routes to methanol and ethanol, as well as to assess if general solid-state pathways to interstellar alcohols exist.

Funds for the support of this study have been allocated by NASA Ames under Interchange No. NCA2-678 and part of the

work was performed when one of us (S. B. C.) held an NAS/NRC Resident Research Associateship at NASA/Ames. This research was carried out during tenure of a Graduate Fellowship from the DOE (M. E. K.) and an SERC grant to the Astrophysics Group at UMIST (T. J. M.). Theoretical studies at NASA/Ames are supported through NASA grant 399-20-

01-30 from the Astrophysics Theory Program (A. G. G. M. T.). We are indebted to the second referee, Barry Turner, for his remarks on the manuscript and for communicating his unpublished observations to us. We are grateful to Michael Mautner for correspondence and to Max Bernstein, Doug Hudgins, and Ant Jones for comments on the manuscript.

REFERENCES

- Agarwal, V., Schutte, W. A., Greenberg, J. M., Ferris, J., Briggs, R., Connor, S., Van de Bult, C. P. E., & Baas, F. 1985, *Origins of Life*, 16, 21
- Andersson, M., Askne, J., & Hjalmarsen, A. 1984, *A&A*, 136, 243
- Askne, J., Höglund, B., Hjalmarsen, A., & Irvine, W. M. 1984, *A&A*, 130, 311
- Blake, G. A., Sutton, E. C., Masson, C. R., & Phillips, T. G. 1987, *ApJ*, 315, 621
- Bohn, R., Allamandola, L. J., & Sandford, S. A. 1995, in preparation
- Brown, P. D., & Charnley, S. B. 1990, *MNRAS*, 244, 432
- Brown, P. D., Charnley, S. B., & Millar, T. J. 1988, *MNRAS*, 231, 409
- Brown, P. D., & Millar, T. J. 1989, *MNRAS*, 240, 25
- Caselli, P., Hasegawa, T. I., & Herbst, E. 1993, *ApJ*, 408, 548
- Cernicharo, J., Kahane, C., Guélin, M., & Gomez-Gonzalez, J. 1988, *A&A*, 189, L1
- Charnley, S. B. 1994, *ApJ*, submitted
- . 1995, in *The Cosmic Dust Connection*, ed. J. M. Greenberg (Dordrecht: Kluwer), in press
- Charnley, S. B., & Millar, T. J. 1994, *MNRAS*, 270, 570
- Charnley, S. B., & Tielens, A. G. G. M. 1992, in *IAU Symp. 150, The Astrochemistry of Cosmic Phenomena*, ed. P. D. Singh (Dordrecht: Kluwer), 317
- Charnley, S. B., Tielens, A. G. G. M., & Millar, T. J. 1992, *ApJ*, 399, L71
- Churchwell, E. 1990, *Astron. Astrophys. Rev.*, 2, 79
- DeFrees, D. J., McLean, A. D., & Herbst, E. 1985, *ApJ*, 293, 236
- Evans, N. J., Lacy, J. H., & Carr, J. S. 1991, *ApJ*, 383, 674
- Friberg, P., Madden, S. C., Hjalmarsen, A., & Irvine, W. M. 1988, *A&A*, 195, 281
- Greenberg, J. M. 1982, in *Comets*, ed. B. Wilkening (Tucson: Univ. of Arizona Press), 131
- Hagen, W., Allamandola, L. J., & Greenberg, J. M. 1979, *Ap&SS*, 65, 215
- Hasegawa, T. I., Herbst, E., & Leung, C. M. 1992, *ApJS*, 82, 167
- Hayashi, M., & Kawada, K. 1974, *Bull. Chem. Soc. Japan*, 47, 3006
- . 1975, *J. Molec. Structure*, 28, 147
- . 1980, *J. Molec. Spectrosc.*, 80, 272
- Herbst, E., & Dunbar, R. C. 1991, *MNRAS*, 253, 341
- Herbst, E., & Leung, C. M. 1989, *ApJS*, 69, 271
- Irvine, W. M., Goldsmith, P. F., & Hjalmarsen, A. 1987, in *Interstellar Processes*, ed. D. J. Hollenbach & H. A. Thronson, Jr. (Dordrecht: Reidel), 561
- Irvine, W. M., Höglund, B., Friberg, P., Askne, J., & Ellder, J. 1981, *ApJ*, 248, L113
- Irvine, W. M., & Schloerb, F. P. 1984, *ApJ*, 282, 516
- Karpas, Z., & Mautner, M. 1989, *J. Phys. Chem.*, 93, 1859
- Lee, H. S., Drucker, M., & Adams, N. G. 1992, *Int. J. Mass. Spectro. Ion Phys.*, 117, 101
- Mangum, J., Plambeck, R. L., & Wootten, A. 1991, *ApJ*, 369, 157
- Mautner, M., & Karpas, Z. 1986, *J. Phys. Chem.*, 90, 2206
- Menten, K. M., Walmsley, C. M., Henkel, C., & Wilson, T. L. 1988, *A&A*, 198, 253
- Millar, T. J., Herbst, E., & Charnley, S. B. 1991a, *ApJ*, 369, 147
- Millar, T. J., MacDonald, G. H., & Habing, R. 1995, *MNRAS*, 273, 25
- Millar, T. J., Olofsson, H., Hjalmarsen, A., & Brown, P. D. 1988, *A&A*, 205, L5
- Millar, T. J., Rawlings, J. M. C., Bennett, A., Brown, P. D., & Charnley, S. B. 1991b, *A&AS*, 87, 585
- Pendleton, Y. J., Tielens, A. G. G. M., & Werner, M. W. 1990, *ApJ*, 349, 107
- Prasad, S. S., & Tarafdar, S. P. 1983, *ApJ*, 267, 603
- Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., Sellgren, K., Tapia, M., & Pendleton, Y. 1991, *ApJ*, 371, 607
- Schutte, W. A. 1988, Ph.D. thesis, Leiden Univ.
- Shimanouchi, T. 1978, *J. Phys. Chem. Ref. Data*, 7, No. 4
- Smith, D. S., Spaniel, P., & Millar, T. J. 1993, *MNRAS*, 266, 31
- Tielens, A. G. G. M. 1992, in *Chemistry and Spectroscopy of Interstellar Molecules*, ed. N. Kaifu (Tokyo: Univ. Tokyo Press), 237
- Tielens, A. G. G. M., & Allamandola, L. J. 1987, in *Physical Processes in Interstellar Clouds*, ed. G. E. Morfill & M. Scholer (Dordrecht: Kluwer), 333
- Tielens, A. G. G. M., & Hagen, W. 1982, *A&A*, 114, 245
- Turner, B. E. 1991, *ApJS*, 76, 617
- van IJendoorn, L. 1985, Ph.D. thesis, Leiden Univ.
- Ziurys, L. M., & McGonagle, D. 1993, *ApJS*, 89, 155

